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Chemical, Thermal, and Light-Driven Reduction of Graphene Oxide: Approach to Obtain Graphene and its Functional Hybrids

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Additional information is available at the end of the chapter

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Abstract

The alternative synthetic route of graphene (G) is presented. At first, graphite is oxidized to graphite oxide, which is dispersed in water to form graphene oxide (GO). GO can be reduced to rGO or G. GO being negatively charged can be used to obtain organic functionalized GO or hybrid of GO, reduction of which finally result in the formation of G-based hybrids. The reduction of GO or GO hybrid can be accomplished by light irradiation, thermal annealing, or by treating with reducing agents. The chemical changed from graphite to GO and GO to rGO can be monitored by surface analysis, microscopic investigation, and various spectroscopic methods.

Keywords: graphene oxide, chemical reduction, photo reduction, graphene hybrids, solution processable graphene, multifunctionality

1. Introduction

Apart from chemical vapor deposition (CVD) or micromechanical exfoliation process, thermal, chemical, or light-driven reduction of graphene oxide (GO) is the simplest route for synthesis of graphene (G) in large scale [1–8]. The light-driven reduction is accomplished through free radical reduction process of GO associated with the decomposition of carboxylic, epoxy, and hydroxyl groups. The chemical reduction process includes reaction of GO with various reducing agents. Depending on the temperature and strength of reducing agent, the extent of reduction of GO or extent of formation of graphene can be varied [2, 3].

G being a hydrophobic material is difficult to be processed in polar solvents especially in water. But for considering chemical reactions or processing with other, ingredient G necessarily needs to be dispersed in solvents [2]. As an alternative route, reduction of GO in the presence of the water soluble polymers such as polyvinylpyrrolidone results in linking between graphene nanosheet and water molecules, making it solution processable [9]. Graphene being unreactive itself can be functionalized by reacting GO with other reagents with subsequent reduction. The synthesis of GO from graphite is usually accomplished by three classical graphite oxidation techniques, including Hummers', Staudenmaier, and Brodie's method [10–12]. The synthesized GO is reduced by light irradiation, high-temperature refluxing, or reacting with reducing agents including hydrazine and its derivatives, ammonia, sodium borohydride, and so on to obtain graphene. To obtain graphene hybrids, GO suspension in water is treated with metallic salts or organic bulk molecules containing amino or sulfonic acid terminals. The formation of chemical bonds or electrostatic bindings stabilizes the resultant GO hybrid, while subsequent reduction results in the formation of G hybrids. The conversions of graphite to GO and GO to G are confirmed from X-ray photo electron spectroscopy (XPS) analysis, Raman spectra, infrared spectra (IR) spectroscopy, and powder X-ray diffraction (PXRD) analysis [2, 13]. The intercalation of materials within graphite results in significant change in chemical and physical properties [14]. The ionic and electronic conductivity can be justified as a function of oxygen content or sp^2 carbon sites. The hybrids usually display multifunctional property including the conductivity of G and additional functionality attributed by the metal ions, semiconductor ingredients, or organic molecules.

The overall process includes three major steps. Firstly, graphite is converted into graphene oxide (GO) by surface oxidation and exfoliation. Secondly, GO is reduced to graphene by reduction. Thirdly, composite of graphene is formed by reaction of GO with metal ions, organic molecules, or semiconductor nanoparticles and subsequent reduction. Multifunctionality can be achieved in the G hybrids formed by this way.

2. Strategy for indirect approach of graphene synthesis

After finding the extraordinary physical, chemical, and mechanical properties, surface area, and optoelectronic characteristics of graphene (G) [13–20], the necessity for chemical and physical modification of G with formation of hybrid materials became a vital issue. Scaffolding of various functional ingredient on G matrices became a facile route for material devising and fabrication. But, due to the hydrophobic nature and chemical inertness, G has been found to be a poor candidate for the as-mentioned purposes. Regarding these facts, GO, the oxidized form of G, became a more potential candidate due to its hydrophilic nature, processability in polar solution and ease for chemical functionalization [21]. Hence, both the theoretical and experimental researches reveal the utilization of G/GO as some applied materials. Though pristine G possesses enormous possibility for various applications, the great opportunity of G or GO primarily is associated with their extent of functionalization and formation of hybrids with other organic and inorganic materials. There exist a number of reports in favor of such strategy. To obtain G through an indirect route, at first GO is obtained

from G. The GO thus synthesized is reduced to form G. For obtaining G-based hybrid, at first GO-based hybrids are obtained from chemical reaction or physical interaction between GO and a second ingredient. The as-prepared GO hybrid is then reduced to form rGO hybrid or the G-based hybrid materials [2, 21]. **Figure 1** represents the scheme for both the approaches.

There exist a number of routes to obtain G. Numerous modified version for synthesis of G, including micromechanical exfoliation, chemical vapor deposition, reduction of GO, or most recently developed electrochemical exfoliation of graphite, are most commonly used [1, 3–6, 22]. Usually, bulk graphite is intercalated by a chemical agent to separate the layers of graphitic stake. Though this process, results contaminated graphitic mass due to the intervened atoms or molecules functioning as impurity, the processes are widely employed for the cheap, nontoxic, and easily affordable ways. In epitaxial growth method, single and multilayer G can be grown using the process for chemical vapor deposition of hydrocarbons on the surface of some metal substrate. Typical thermal decomposition of Si also can be utilized. The micromechanical cleavage is the most facile techniques to isolate pure G from graphite. All these methods are suitable for separation of single-layer G, which is chemically very stable. The problem with this very pure form of G is its limited chemical affinity for a second chemical entity, metal ions, semiconductor ingredient, metal complex, or bulk organic molecules. However, the purpose of the addition of such an entity is to decorate a second functionality in the hybrid in addition to the conductivity and stability of G. G is composed of the sp^2 hybridized carbon atoms. The perpendicular electronic currents that circulate above and below the planar network of graphite layers are very stable and difficult to be destroyed. Also, it is not facile to generate defect sites in G, which can aid chemical bond formation with other ingredient.

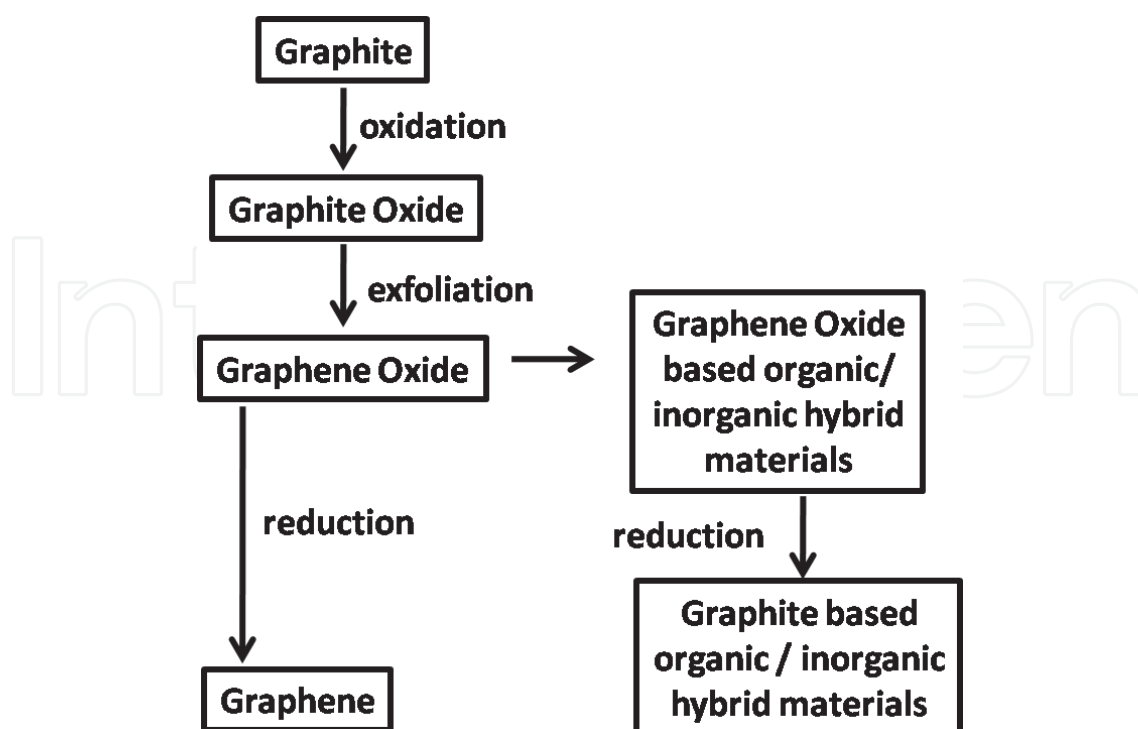


Figure 1. Scheme for the indirect synthesis of G and G-based organic/inorganic hybrid materials.

These intrinsic limitations can be overcome by a three-step process. Firstly, graphite materials are chemically converted into GO. Then, the GO is used for making chemical bond or physical attachments with active functional ingredient. Finally, the hybrids are reduced to form G-based complex structures. Initially for graphite \rightarrow GO conversion, the conductivity of G is destroyed significantly due to the destruction of sp^2 conductive π networks. The sites where oxygen atoms become attached to G take the form of sp^3 hybridized carbon [23, 24]. But due to the attachment of oxygenated sites at G basement, the chemical affinity is increased. Thus, the presence of oxygenated sites in terms of epoxy, hydroxyl, and carboxyl groups increases the possibility of chemical reaction or physical affinity of GO toward other functional ingredients. Hence, the formation of GO-based nonconductive inorganic hybrid materials (GO-M) takes place in the second stage. In the final stage, GO-M is reduced to form rGO-M or G-M type hybrid. During reduction, the oxygenated sites scaffolding M remain unaffected, whereas the rest of the bare functional sites is reduced to recover some of graphene's conductivity and other functionality. The G-M hybrid thus possesses the functionality of both G and M [21].

3. Oxidation of graphite to GO with subsequent reduction to graphene

Graphite usually can be oxidized by Hummers', Staudenmaier, and Brodie's method (**Figure 2**). The typical synthetic routes involved are as following:

3.1. Hummers method

In Hummers' method, 1.0 g graphite powder, 1.0 g finely meshed $NaNO_3$, and 50 mL 97% H_2SO_4 need to be cooled to $0^\circ C$ by stirring in an ice bath for 15 min [10]; 3.0 g finely meshed $KMnO_4$ powder needs to be added slowly with vigorous stirring with maintaining the temperature of the mixture below $20^\circ C$. After 30 min, the mixture needs to be warmed to $35^\circ C$ for 30 min. Then, 200 mL water should be added slowly. The temperature will rise gradually in this stage and it should be maintained around $95^\circ C$ for another 30 min. Then, 400 mL water and 12 mL 30% H_2O_2 must be added with stirring. The mixture

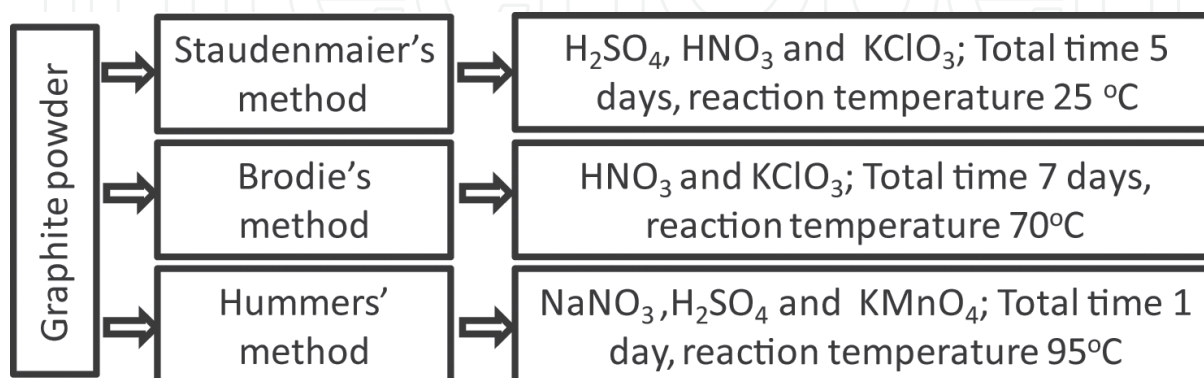


Figure 2. Scheme for the various graphite oxidation techniques through slight modification to reported classical methods.

needs to be centrifuged at 3000 rpm for 10 min. The precipitate should be washed one time with 5% HCl solution and three times with water. The precipitate finally needs to be dried at 70°C for 24 hours to obtain H-GO.

3.2. Staudenmaier method

In Staudenmaier process, a mixture of 35 mL H_2SO_4 (95–98%) and 18 mL fuming HNO_3 in a round bottom flask need to be cool down to 0°C by stirring in an ice bath [11]. Then, 2 g graphite will be added to the mixture under vigorous stirring to obtain a homogeneous dispersion. While keeping the reaction flask in the ice bath, 22 g KClO_3 must be added slowly (over 15 min) to the mixture in order to avoid any sudden rise in temperature and formation of explosive chlorine dioxide (ClO_2) gas. After complete dissolution of KClO_3 , the reaction flask will be removed from the ice bath with capping loosely to allow evolution of gases. The mixture must be stirred vigorously for 5 days at room temperature. After completion of the reaction, the mixture should be poured into 2-L deionized water and filtered after keeping overnight for sedimentation. The precipitate thus obtained should be dispersed and stirred repeatedly by HCl (5%) solutions to remove sulfate ions. The mass obtained will be washed several times with deionized water until neutral pH of the filtrate is obtained. The suspension obtained should be dried in a vacuum oven at 60°C for 48 h to obtain S-GO.

3.3. Brodie's method

In Brodie's method, 6 g graphite powder should be meshed finely with 21 g KClO_3 in a retort. The powdered mixture might be poured into a round bottom flask fitted with magnetic stirrer [12], and 75 ml fuming HNO_3 needs to be added to the mixture with stirring continuously at 70°C for 1 day until the disappearance of yellow vapor. The mixture obtained thus should be washed repeatedly with water. The final product will be obtained from drying. The whole procedure was repeated three times by Brodie using the final products of the former operation as the starting materials for the consecutive operation.

4. Reduction of GO into rGO or graphene

The oxygenated functional groups of GO disappear due to the reduction. For mild reduction, there exist some residual oxygenated sites. This form is usually presented by rGO. In fact, during treatment with strong reducing agent, rGO sometimes contains insignificant amount of oxygenated sites and reveal similar characteristics of G. The as-prepared G displays some electronic and chemical properties, which are comparable with pristine G. In general, oxygen presents on GO is available mainly in the forms of epoxy (the bridge site oxygen) and hydroxyl ($-\text{OH}$ groups) and carboxylic acid ($-\text{COOH}$) groups. The relative composition in terms of C:O:H ratio varies according to the synthetic route, degree of oxidation, and variations in the synthesis conditions. In average, the percent of oxygen in GO remains around 30% by weight. To remove these oxygenous sites, GO can be reduced through several ways including: (1) thermal reduction, (2) photo reduction, and (3) chemical reduction.

4.1. Thermal reduction

Thermal reduction of GO is a simple heating process accomplished by gradual heating of solid GO mass or its dispersion in solvents under inert atmosphere. The absence of oxygen and reactive chemical species needs to be ensured as it might result in the loss of carbon content due to the formation of gases or volatile substances. Gradual decrease in weight loss in thermogravimetric analysis indicates the decomposition of oxygenated functional groups and conversion of GO into rGO or G. Complete reduction of GO by heat treatment is possible, and the process is defined as thermal annealing reduction. Fast heating of GO at a rate above $2000^{\circ}\text{C min}^{-1}$ results in the exfoliation of graphite oxide into G. Such exfoliation of the stacked GO mass is aided by the swift expansion of CO or CO_2 gases evolved at the interlayer space of G sheets due to the fast heating of GO. At high temperature, the oxygenous groups decompose, and the gases make very high pressure within the layers. Calculations show that at 300 and 1000°C , a pressure of 40 and 130 MPa, respectively, is created on the surface of G. However, a pressure of only 2.5 MPa is enough to separate two stacked GO platelets. Thus, the rapid heating process not only exfoliates GO but also reduces the functionalized graphene sheets by decomposing oxygen-containing groups at high temperature. Due to these multiple effects, thermal reduction of GO is preferred over other methods to generate G. In spite, this procedure reveals some drawback, as it can produce small sized and wrinkled graphene sheets only. This is mainly because the decomposition of oxygen-containing groups is associated with the removal of some carbon atoms from the G skeleton. However, ultimately chopping of the large-sized G sheets into tiny pieces also results in the distortion in morphology of carbon skeleton (**Figure 3**). The thermal annealing also generates defects and damages at the structure of G due to the evolution of CO_2 gas. Around 30% weight loss takes place during the conversion of GO into G. Although the G obtained is very pure, the electronic property of rGO-based G decreases significantly compared with G obtained from CVD method. Such incident takes place due to the decrease in ballistic transport path length and introduction of scattering centers. The electrical conductivity of rGO-based G is around $10\text{--}23\text{ S cm}^{-1}$, which is significantly lower than that of perfect G. The thermal reduction of GO at liquid phase results in larger sized G [25]. In this method, the thermal treatment is applied after fabricating macroscopic films, powders or thin pellets.

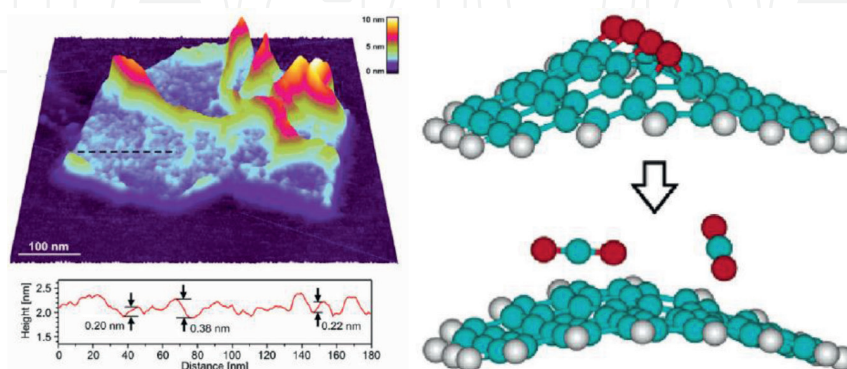


Figure 3. Three dimensional representation of a $600\text{ nm} \times 600\text{ nm}$ AFM scan of a G nanosheet obtained from heat treatment of GO. It shows the wrinkled and rough structure of the surface.

4.2. Photo reduction

The photo-aided reduction is usually performed in solution state. Exfoliated GO water solution in a vial is needed to be irradiated by 365 nm light beam flashed from a 500 W high-pressure Hg lamp. Typically, 99.99% H₂ or N₂ at 1 atm pressure needs to be flown through a quartz cell-filled GO sample at a rate of about 50 mL/min. The light intensity can be about 67 mW/cm², and the light source can be positioned at a distance of about 40 cm from the sample surface. The degree and extent of GO → rGO/G conversion can be controlled by tuning the exposure time. Photoreduction can also be resulted in by employing a UV cutoff filter (<420 nm) to generate visible light irradiation. But, in such condition, the degree of reduction becomes low. In contrast, UV irradiation obtained from a visible-light cutoff filter (>390 nm) can cause in photoreduction through the same extent of reduction taking place in absence of any filter. Thus, UV irradiation has been found to be a very effective way to reduce GO. Light irradiating reduction can also be accomplished using an intense light source such as laser or photocatalyst such as TiO₂ or ZnO.

Light-driven reduction takes place through a mechanism associated with free radical cleavage method. Epoxy groups locating at the basal planes of GO are relatively unstable due to the bond strain and angular distortion associated with the bending of regular sp₃ hybrid orbitals. In the reduction process, π - π^* electronic excitations within the sp₂ domains on the GO surface take place as the initial step of UV irradiation. The electron-hole pairs generated this way, then migrates to the epoxy groups and aids C—O—C bond breaking process. Associated release of O₂ and formation of larger sp₂ domains take place simultaneously. It was found that some ions including Ag⁺ can promote the destruction of the C—O bond and escaping of O₂ during photoreduction. In this case, the reduction of GO takes place along with the formation of Ag nanoparticles from Ag⁺ under the presence of ethylene glycol and NaBH₄. Here, some strong interaction happens between Ag nanoparticles and the remaining surface hydroxyl O atoms. The reduction of GO can initially be justified by change in color of GO dispersion and respected UV-vis spectra (**Figure 4**). The epoxy bond cleavage study of X ray photo electron spectra suggests that the extent of reduction of oxygenated sites follows the trend as epoxy > ketonic > carboxylic > hydroxyl groups.

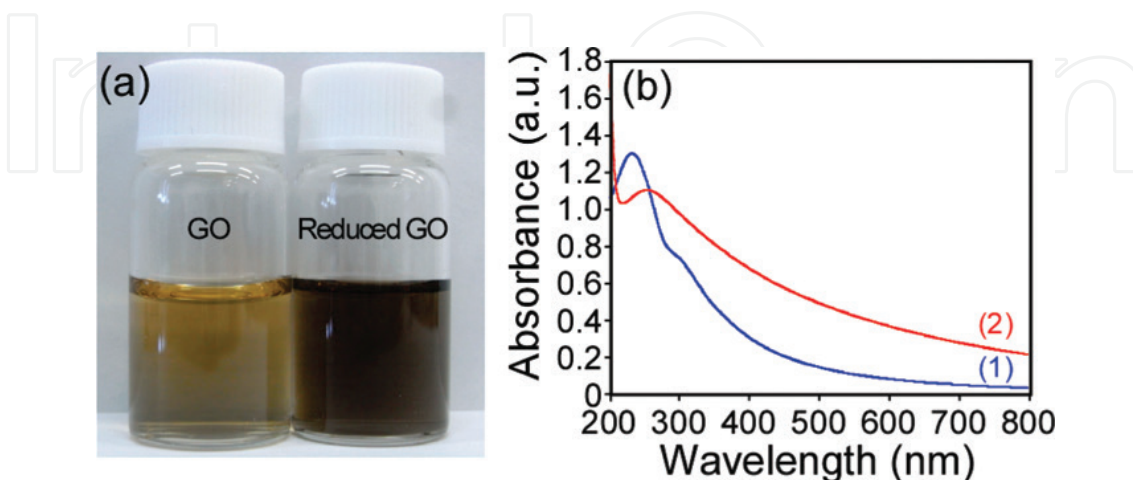


Figure 4. (a) Change in color and (b) UV-vis spectra of dispersion of GO (1) and rGO (2) generated from photoreduction of GO in H₂ for 2 h. The color turns to black after photoreduction.

4.3. Chemical reduction

A list of reducing agent can be used for the reduction of GO chemically. Typical strong reducing agent includes hydrazine, dimethylhydrazine and other related derivatives, sodium borohydrate (NaBH_4), ammonia, hydrogen plasma and so on. Depending on the strength of chemical agent, the reduction can be accomplished from room temperature to elevated temperature. The commonest way of chemical reduction is treating GO with hydrazine hydrate at 100°C for 24 hours [26]. Instead of the solution phase, GO film can be exposed to hydrazine vapor from long to short time to obtain desired extent of reduction. In average, the conductivity of rGO films obtained from hydrazine reduction is 99.6 S cm^{-1} with a C/O ratio of around 12.5 [27]. Strong metal hydride reducing agent, including sodium hydride, sodium borohydride (NaBH_4), and lithium aluminum hydride, cannot be applied through facile way as these reducing agents exhibit slight to very strong reactivity toward water. As water is the major dispersion phase for GO, the presence of water cannot be avoided.

NaBH_4 hydrolyzes in water through a slow rate. As a result, compared with hydrazine solution, freshly prepared NaBH_4 solution serves as a more effective reducing agent for reducing C=O groups in GO [28]. However, the efficiency of NaBH_4 is low to moderate for reduction of epoxy, carboxylic acids, and alcohol groups. To solve this problem after reduction with NaBH_4 , dehydration with concentrated sulfuric acid (98%) at 180°C can be applied to reduce the oxygenated sites. Thus, reaching to a C/O ration of 8.6 with conductivity value as 16.6 S cm^{-1} is possible [29]. Ascorbic acid (Vitamin C) as a comparatively water stable and nontoxic materials can reduce GO with a C/O ration of 12.5 and conductivity as 77 S cm^{-1} . Glucose solution at 100°C can also be applied for the reduction of GO. Exposure to hydrogen plasma for several seconds is the shortest time reduction route. Heating GO with urea as a simple and affordable method. Reduction of GO by HI is possible in various physical condition such as GO colloid, powder, or film [30]. Some other mild reducing agent for GO includes hydroquinone, pyrogallol, hot strong alkaline solutions (KOH, NaOH), hydroxylamine, and thiourea.

5. Formation of GO hybrid

5.1. Scaffolding metal/metal oxide or bulk molecules through physical entrapments to form GO-M hybrid

The columbic interaction between the negatively charged GO nanosheet and positively charged chemical ingredients including metal ions function as the major driving force behind the formation of this type of hybrid (**Figure 5**). Initially, some primary metal ions bound to some of the partially charged oxygenated sites of GO nanosheets and prohibit these sites from further reaction with other metal ions. The GO nanosheet thus losses its charge, becomes heavier, and precipitates as sediments in the form of GO-M hybrid. The GO-M hybrid then can be converted to G-M hybrid by means of chemical, thermal, or photo reduction. When GO-M hybrid is reduced to G-M, along with the change of $\text{GO} \rightarrow \text{G}$, the growth of metal precursor takes place by gradual combination with oxygen atoms, metal oxide molecules (produced during reduction process), and more free metal ions. As a result, in the final stage,

irregular-shaped metal oxide nanoparticles become anchored to the rGO matrices, which in fact function as hybrid of G with metal/ metal oxide.

5.2. Functionalization of GO by organic compounds to form GO-Org hybrids

Numerous G-based hybrid materials can be generated from organic functionalization of GO (GO-Org) and its successive reduction process. In the form of GO-Org, the materials show excellent solubility and solution processability in both the water and organic solvents. As G-Org form is inferior with respect to these properties, prior to the formation of G-Org, a common stand includes obtaining GO-Org as the earlier step. At the second step, the GO-Org is reduced to G-Org through a suitable reduction process discussed above. Most of the outstanding properties of G and the organic molecules sustain in G-Org without being perturb. The durability, stability, and extent of functionality have been found to be excellent. Both the noncovalent and covalent functionalization of GO with organic compounds thus became the subject of intensive research for developing G-based hybrid nanocomposites with new functions and applications. From noncovalent aspect, due to the tendency of GO for forming π - π and hydrophobic interaction, strong adsorption between organic aromatic compounds or bulk molecules and GO nanosheets takes place. Thus, the formation of numerous GO-Org hybrids becomes possible. For covalent modification, the oxygenated sites in GO serve as the active site toward various chemical agent. Such reaction needs some pre-requisite condition including the perfect diffusion of the organic precursors toward the reactive moiety of GO nanosheet with successful approach for undergoing surface reactions. A wide range of organic compounds including polyanilines, phenolic derivatives, porphyrins, aromatic dyes, alkylamines, doxorubicin, hydrochloride, ionic liquids, pyrene, perylenedimide, cyclodextrin, tetracyanoquinodimethane, and aryl diazonium compounds can react

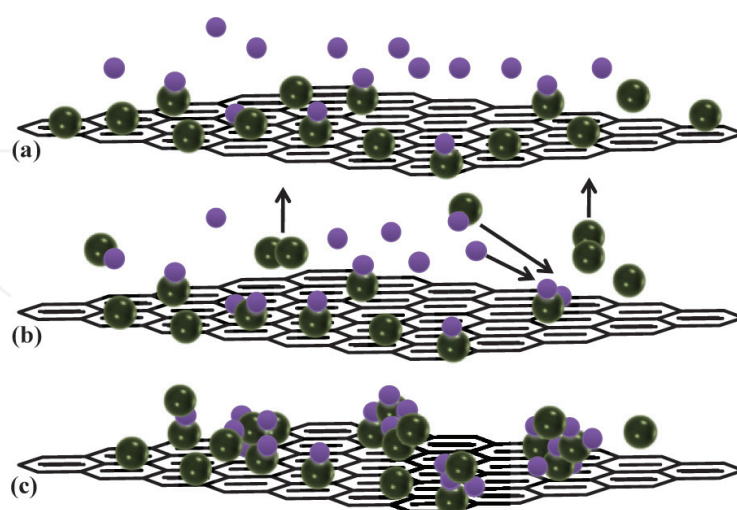


Figure 5. Scheme for the formation of rGO-metal oxide nanoparticle hybrids. (a) In the first step, negatively charged oxygenated site (deep green) of GO electrostatically attracts some primary metal ions (violet) through columbic force. (b) In the second step, reduction takes place. During reduction, some oxygen escapes from the system, whereas metal-masked oxygenated sites remain unreduced and attract metal oxide precursors, oxygen, and further metal ions. (c) Gradual deposition finally results irregular-shaped metal oxide nanoparticles anchored on rGO matrices [21].

noncovalently or covalently for being attached on GO surface. Prior to the conversion of G-Org hybrid, additional facilities obtained from the formation of GO-Org hybrid include the increase in the dispersibility due to the existence of residual polar groups (after some being engaged for chemical bonding with the organic molecules) in GO-Org.

6. Monitoring the graphite \rightarrow GO \rightarrow G conversion and characterization of the products

The black-colored graphite powder changes to stake layered mass in graphite oxide. Color of GO dispersion in water is usually brown, though this color varies according to the route of oxidation. GO dispersion in water turns to black-colored coagulated nanosheet due to the reduction (**Figure 6**). Although these changes in morphology are visible by bare eyes, there exist numerous well characterized physical and chemical methods to monitor the changes. The surface morphology can be characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM). In case of hybrid formation with metallic ingredients, TEM in combination with EDX becomes an excellent characterization tool. The granular pattern and changes in interlayer distances with reaction can be monitored by powder X-ray diffraction (PXRD) study. The incorporation of oxygenated groups can be monitored by Raman spectra. The extent of oxygenation and nature of functional groups can be justified by infrared spectra (IR), and finally, the presence of various functional groups can be confirmed from X-ray photo electron spectroscopy (XPS).

When graphite powder is oxidized into GO, the intercalation of oxygenated groups separate layers of graphite. But, the hydrophilic functional groups at the graphitic surface make the sheet coagulated with each other. The graphite oxide thus seems to be some massive pellets. When graphite oxide is ultrasonicated in water, the nanosheets become separated and sustain in water as colloid. The colors of the GO solutions vary depending on the synthetic route (**Figure 6**). The color change is also remarkable during the formation of GO to GO-M and finally from GO-M to G-M form. In **Figure 6** (h–j), the brown-colored GO starts to precipitate due to the mixing of CoCl_2 solution. When GO-Co is reduced by hydrazine, the final color of G-Co becomes dark. Change in PXRD pattern (**Figure 6k**) clearly depicts that due to oxidation, the interlayer distance of graphite increases significantly. The extension of oxygenated groups from the graphitic basal plane is responsible for such observation. Graphite usually show characteristic sharp peak around 27° (2θ), which represents the reflection plane (0 0 1) of graphite and indicates its amorphous structure [31]. Due to oxidation, the graphitic sharp peak disappears and appearance of relatively wider peak around $2\theta = 9.13, 11.4$, and 11.6 for H-GO, S-GO, and B-GO, respectively, represent the lowering of reflection planes. In this case, the 'd-spacing' values become as 9.68, 7.76, and 7.62 Å, respectively. When GO is reduced to G, the wide peak disappears and a broad hollow rises around 20° (2θ).

Raman spectroscopy is commonly employed to monitor change and doping on graphitic materials and GO. Raman spectra of carbon materials show two bands at $\sim 1580\text{ cm}^{-1}$ (G band) and $\sim 1350\text{ cm}^{-1}$ (D band; **Figure 7a**). These G and D bands are responsible for E_{2g} photon

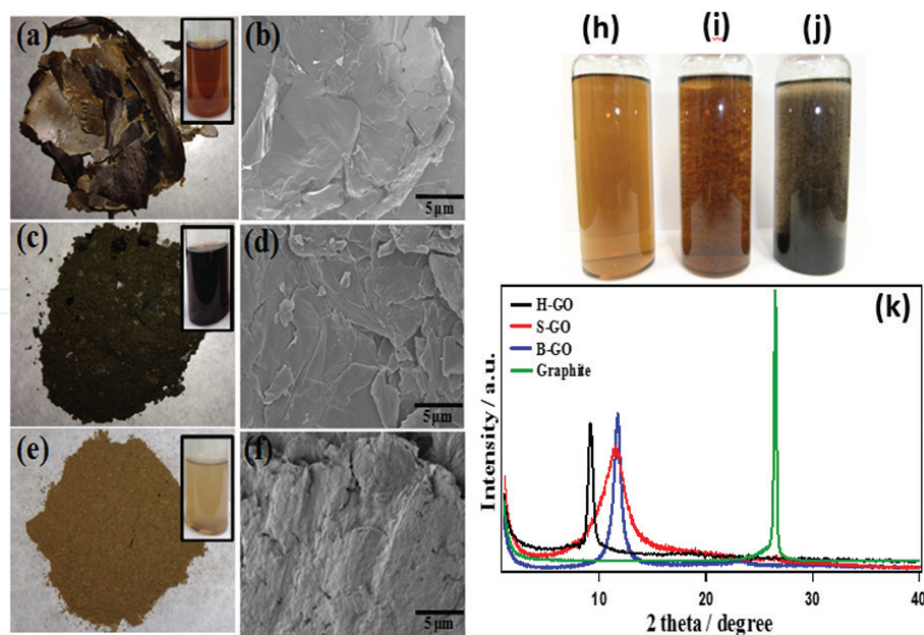


Figure 6. Physical properties and morphologies of the samples. Photographs of GO prepared from Hummers' method (H-GO) (a), Staudenmaier method (S-GO) (c), and Brodie's method (B-GO) (e). The inset images show the respective solution (1 mg/mL) in water after ultrasonication for 2 h. Respective SEM images of H-GO (b), S-GO (d), and B-GO (f) display their surface morphologies. (h)–(j) The change in color and physical state of GO solution, GO-M hybrid and G-M hybrid (M represents the Co^{2+} ion). (k) The powder X-ray diffraction patterns of graphite powder, H-GO, S-GO, and B-GO [35].

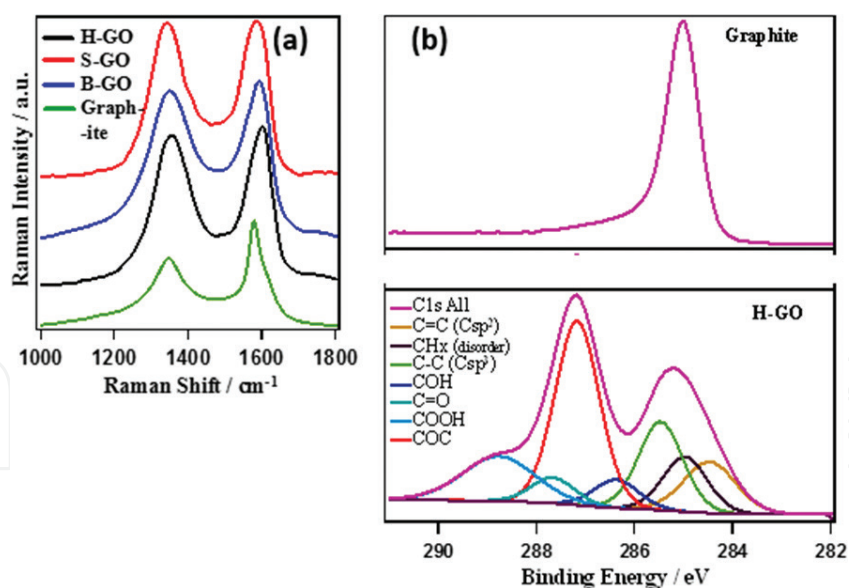


Figure 7. (a) Raman spectra and (b) XPS spectra of graphite and GO synthesized by various routes. GO shows characteristic oxygenous functional groups.

corresponding to sp_2 atoms and κ -point photon of A_{1g} symmetry of breathing mode resulting from local defects and disorder [32, 33]. During chemical conversion, the hole and electron doping in carbon materials results in the shifting of G-band, as well the intensity ratio

of D and G-band varies significantly with doping. Peak ratio (I_D/I_G) gradually increases for $G \rightarrow GO$; however, decreases along the conversion: $GO \rightarrow GO/GO\text{-metal ion hybrids} \rightarrow G/G\text{-metal oxide hybrids}$. The I_D/I_G value changes proportionally with the extent of sp_2 domain [34, 35]. Thus, the gradual decrease in I_D/I_G value implies expansion of this domain. The expansion of sp_2 domain indicates conversion of GO to G, whereas shrinking in this value signifies conversion of G to GO.

XPS is the most powerful tool for marking the oxidation of graphite into GO and reduction of GO into G. Pure graphite shows a sharp peak arising from the sp_2 hybridized carbon atoms. After oxidation, all the samples exhibit two individual peaks near 285 and 287 eV in their XPS spectra [36–38]. The deconvolution of spectra shows that GO exhibits characteristic peaks comprising several particular oxygenated functional groups. The existence of epoxide ($-\text{O}-$) and hydroxyl ($-\text{OH}$) groups at 286.8–287.0 eV, and carbonyl ($-\text{C}=\text{O}$) and carboxyl ($-\text{COOH}$) groups at 287.8–288.0 and 289.0–289.3 eV, respectively, confirms the presence of oxygenated sites in GO and graphite \rightarrow GO conversion (**Figure 7b**). When GO is reduced into rGO or G, the peak intensity gradually reduces depending on the extent of reduction. For complete reduction, the spectra take the pattern of graphite almost, except revealing the existence of some residual oxygenated sites [39–41].

7. Conclusions

Indirect method for synthesis of graphene includes conversion of graphite into graphite oxide and GO dispersion by various oxidation method including Hummers', Staudenmaier, and Brodie's techniques with successive reduction into rGO. The graphite oxide synthesized can be dispersed into water by ultrasonication to obtain GO solution. Finally, the GO treating for reduction by means of thermal, photo irradiation, or chemical method can transform into rGO or G. In addition, GO having higher chemical affinity than G can easily be used for the formation of various functional GO hybrids, successive reduction of which can result in the formation of G-based hybrid materials. The series of chemical changes and progress of the reactions can be monitored by various surface analysis techniques and spectroscopic investigations.

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References

- [1] Eda G., Fanchini G., Chhowalla M. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nat. Nanotechnol.* 2008;3:270–274.
- [2] Zhu Y., Murali S., Cai W., Li X., Suk J.W., Potts J.R., Ruoff R.S. Graphene and graphene oxide: Synthesis, properties, and applications. *Adv. Mater.* 2010;22:3906–3924.
- [3] Sutter P.W., Flege J.I., Sutter E.A. Epitaxial graphene on ruthenium. *Nat. Mater.* 2008;7:406–411.
- [4] Lee Y., Bae S., Jang H., Jang S., Zhu S.E., Sim S.H., Song Y.I., Hong B.H., Ahn J.H. Wafer-scale synthesis and transfer of graphene films. *Nano Lett.* 2010;10:490–493.
- [5] Hernandez Y., Nicolosi V., Lotya M., Blighe F.M., Sun Z.Y., De S., McGovern I.T., Holland B., Byrne M., Gun'ko Y.K., Boland J.J., Niraj P., Duesberg G., Krishnamurthy S., Goodhue R., Hutchison J., Scardaci V., Ferrari A.C., Coleman J.N. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nat. Nanotechnol.* 2008;3:563–568.
- [6] Wang J.Z., Manga K.K., Bao Q.L., Loh K.P. High-yield synthesis of few-layer graphene flakes through electrochemical expansion of graphite in propylene carbonate electrolyte. *J. Am. Chem. Soc.* 2011;133:8888–8891.
- [7] Shih C.J., Vijayaraghavan A., Krishnan R., Sharma R., Han J.H., Ham M.H., Jin Z., Lin S.C., Paulus G.L.C., Reuel N.F., Wang Q.H., Blankshtein D., Strano M.S. Bi- and trilayer graphene solutions. *Nat. Nanotechnol.* 2011;6:439–445.
- [8] Liu N., Luo F., Wu H.X., Liu Y.H., Zhang C., Chen J. One-step ionic-liquid-assisted electrochemical synthesis of ionic-liquid-functionalized graphene sheets directly from graphite. *Adv. Funct. Mater.* 2008;18:1518–1525.
- [9] Zhang Y., Hu W., Li B., Peng C., Fan C., Huang Q. Synthesis of polymer-protected graphene by solvent-assisted thermal reduction process. *Nanotechnology* 2011;22:34.
- [10] Hummers W.S., Offeman R.E. Preparation of graphitic oxide. *J. Am. Chem. Soc.* 1958;80:1339–1339.
- [11] Staudenmaier L. Verfahren zur darstellung der graphitsäure. *Ber. Dtsch. Chem. Ges.* 1898;31:1481–1487.
- [12] Brodie B.C. On the atomic weight of graphite. *Philos. Trans. R. Soc. Lond.* 1859;149:249–259.
- [13] Land T.A., Michely T., Behm R.J., Hemminger J.C., Comsa G. STM investigation of single layer graphite structures produced on Pt(111) by hydrocarbon decomposition. *Surf. Sci.* 1992;264:261–270.
- [14] Dresselhaus M.S., Dresselhaus G. Intercalation compounds of graphite. *Adv. Phys.* 2002;51:1–186.

- [15] Nagashima A., Nuka K., Itoh H., Ichinokawa T., Oshima C., Otani S. Electronic states of monolayer graphite formed on TiC(111) surface. *Surf. Sci.* 1993;291:93–98.
- [16] Van Bommel A.J., Crombeen J.E., van Tooren A. LEED and Auger electron observations of the SiC(0001) surface. *Surf. Sci.* 1975;48:463–472.
- [17] Forbeaux I., Themlin J.-M., Debever J.M. Heteroepitaxial graphite on 6H-SiC(0001): Interface formation through conduction-band electronic structure. *Phys. Rev. B* 1998;58:16396–16406.
- [18] Berger, C., Song Z., Li T., Li X., Ogbazghi A.Y., Feng R., Dai Z., Marchenkov A.N., Conrad E.H., First P.N., De Heer W.A. Ultrathin epitaxial graphite: 2D electron gas properties and a route toward graphene-based nanoelectronics. *J. Phys. Chem. B* 2004;108:19912–19916.
- [19] Berger C., Song Z., Li X., Wu X., Brown N., Naud C., Mayou D., Li T., Hass J., Marchenkov A.N., Conrad E.H., First P.N., de Heer W.A. Electronic confinement and coherence in patterned epitaxial graphene. *Science* 2006;312:1191–1196.
- [20] Ohta T., Bostwick A., Seyller T., Horn K., Rotenberg E. Controlling the electronic structure of bilayer graphene. *Science* 2006;313:951–954.
- [21] Karim M.R., Shinoda H., Nakai M., Hatakeyama K., Kamihata H., Matsui T., Taniguchi T., Koinuma M., Kuroiwa K., Kurmoo M. et al Electrical conductivity and ferromagnetism in a reduced graphene-metal oxide hybrid. *Adv. Funct. Mater.* 2013;23:323–332.
- [22] Ambrosi A., Pumera M. Electrochemically exfoliated graphene and graphene oxide for energy storage and electrochemistry applications. *Chem. Eur. J.* 2016;22:153–159.
- [23] Kudin K.N., Ozbas B., Schniepp H.C., Prud'homme R.K., Aksay I.A., Car R. Raman spectra of graphite oxide and functionalized graphene sheets. *Nano Lett.* 2007;8:36–41.
- [24] Das A., Pisana S., Chakraborty B., Piscanec S., Saha S.K., Waghmare U.V., Novoselov K.S., Krishnamurthy H.R., Geim A.K., Ferrari A.C., Sood A.K. *Nat. Nanotechnol.* 2008;3:210.
- [25] Zhao J., Pei S., Ren W., Gao L., Cheng H.-M. Efficient preparation of large-area graphene oxide sheets for transparent conductive films. *ACS Nano* 2010;4:5245–5252.
- [26] Kovtyukhova N.I., Wang Y., Berkdemir A., Cruz-Silva R., Terrones M., Crespi V.H., Mallouk T.E. Non-oxidative intercalation and exfoliation of graphite by Brønsted acids. *Nat. Chem.* 2014;6:957–963.
- [27] Fernandez-Merino M.J., Guardia L., Paredes J.I., Villar-Rodil S., Solis-Fernandez P., Martinez-Alonso A., et al Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions. *J. Phys. Chem. C* 2010;114:6426–6432.
- [28] Shin H.-J., Kim K.K., Benayad A., Yoon S.-M., Park H.K., Jung I.-S., et al Efficient reduction of graphite oxide by sodium borohydride and its effect on electrical conductance. *Adv. Funct. Mater.* 2009;19:1987–1992.
- [29] Gao W., Alemany L.B., Ci L., Ajayan P.M. New insights into the structure and reduction of graphite oxide. *Nat. Chem.* 2009;1:403–408.

- [30] Moon K., Lee J., Ruoff R.S., Lee H. Reduced graphene oxide by chemical graphitization. *Nat. Commun.* 2010;1:73–78.
- [31] Cai, D., Song M. Preparation of fully exfoliated graphite oxide nanoplatelets in organic solvents. *J. Mater. Chem.* 2007;17:3678–3680.
- [32] Tuinstra F., Koenig J.L. Raman spectrum of graphite. *J. Chem. Phys.* 1970;53:1126.
- [33] Ferrari A. C., Robertson J., Interpretation of raman spectra of disordered and amorphous carbon. *Phys. Rev. B* 2000;61:14095.
- [34] Hatakeyama K., Karim M.R., Ogata C., Tateishi H., Funatsu A., Taniguchi T., Koinuma M., Hayami S. and Matsumoto Y. Proton conductivities of graphene oxide nanosheets: single, multilayer, and modified nanosheets. *Angew. Chem., Int. Ed.* 2014;53:6997–7000.
- [35] Karim M.R., Islam Md.S., Hatakeyama K., Nakamura M., Ohtani R., Koinuma M. and Hayami S. Effect of interlayer distance and oxygen content on proton conductivity of graphite oxide. *J. Phys. Chem. C* 2016;120:21976–21982.
- [36] Ikeda Y., Karim M.R., Takehira H., Matsui T., Taniguchi T., Koinuma, Matsumoto Y. and Hayami S. Proton conductivity of graphene oxide hybrids with covalently functionalized alkylamines. *Chem. Lett.* 2013;42:1412–1414.
- [37] Ikeda Y., Karim M.R., Takehira H., Hatakeyama K., Taniguchi T., Koinuma M., Matsumoto Y. and Hayami S. Impaired proton conductivity of metal-doped graphene oxide. *Bull. Chem. Soc. Jap.* 2014;87:639–641.
- [38] Hatakeyama K., Karim M.R., Ogata C., Tateishi H., Taniguchi T., Koinuma M., Hayami S. and Matsumoto Y. Optimization of proton conductivity in graphene oxide by filling sulfate ions. *Chem. Commun.* 2014;50:14527–14530.
- [39] Wakata K., Karim M.R., Islam Md.S., Ohtani R., Nakamura M., Koinuma M. and Hayam S. Superionic Conductivity in Hybrid of 3-hydroxypropanesulfonic acid and graphene oxide. *Chem. Asian J.* 2017; 12:194–197.
- [40] Hatakeyama K., Tateishi H., Taniguchi T., Koinuma M., Kida T., Hayami S., Yokoi H. and Matsumoto Y. Tunable graphene oxide proton/electron mixed conductor that functions at room temperature. *Chem. Mater.* 2014;26:5598–5604.
- [41] Hatakeyama K., Islam Md.S., Koinuma M., Ogata C., Taniguchi T., Funatsu A., Kida T., Hayami S. and Matsumoto Y. Super proton / electron mixed conduction in graphene oxide hybrids by intercalating sulfate ions. *J. Mater. Chem. A* 2015;3:20892–20895.

